[0006]

However, with this method, fusion and kneading are carried out intentionally at a low temperature in order to restrain the generation of spherical crystals and to form a network structure, so that the melt viscosity will be high, thereby necessitating reduction of the polymer concentration to lower the viscosity depending on the extruder. Also, since the form of the porous film structure is keenly influenced by the melting temperature, a temperature management precision is highly demanded.

[0007]

On the other hand, a hydrophobic polymer such as PVDF has a low hydrophilic property, so that when this is used as a separation film, there is raised a problem such that solid substances such as fine particles and protein contained in feed water tend to adhere onto the film surface and the adhering substancese can hardly be removed. For this reason, a method for hydrophilization of a PVDF porous film is proposed. There is known a method in which, after a PVDF porous film is wetted with a solvent, the resultant is brought into contact with a solution containing polyvinylpyrrolidone and a polymerization initiator, followed by heating to cross-link the polyvinylpyrrolidone (for example, see Japanese Patent Application Laid-Open (JP-A) No. 11-302438). However, with such a method that accompanies cross-linking or polymerization of a hydrophilic substance, the production steps will be complex, thereby raising problems such as being disadvantageous in terms of costs.

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0008]

Therefore, an object of the present invention is to provide a production method for preparing a porous film of a poly(vinylidene fluoride) based resin which has a microstructure providing a satisfactory mechanical strength and permeation performance and is improved in hydrophilic property, without the precise control of temperature before cooling, as well as a porous film prepared by the above method.

MEANS FOR SOLVING THE PROBLEMS

[0009]

In order to achieve the aforementioned object, the present inventors have made an eager research on a hydrophilization process of a porous film made of a poly(vinylidene fluoride) based resin and the control of a microstructure, and have found out that the aforementioned object can be achieved by dispersing an organized clay into a liquid raw material at the time of forming a film by the thermally induced phase separation method, thereby completing the present invention.

[0010]

Namely, the method of producing a porous film of the present invention is a method for producing a porous film wherein a porous

film of a poly(vinylidene fluoride) based resin is prepared by dissolving the poly(vinylidene fluoride) based resin in a poor solvent through heating to form a liquid raw material for a film, and then cooling the liquid raw material at temperature of 170°C or above to bring about a phase separation, characterized in that an organized clay being organized by a hydrophilic compound is dispersed in said liquid raw material for a film in an amount of 1 to 25 parts by weight relative to 100 parts by weight of the poly(vinylidene fluoride) based resin.

[0011]

With respect to the control of the structure of a porous film in the thermally induced phase separation method, in the case of a poly(vinylidene fluoride) based resin, in order to form a structure in which irregularly shaped resin phases are linked like a network, precise control of the melting temperature of the poly(vinylidene fluoride) based resin has been necessary, as disclosed in WO99/47593 Gazette. Typically, this temperature is set to be a little lower than the complete homogeneous melting temperature. It seems that a phenomenon of formation of a microstructure in which resin phases are linked in a three-dimensional manner occurs by melting at a little low temperature of a specific range so that the crystals may not grow coarse more than needed in a crystal growth process accompanying the cooling. In the present invention, by dispersing an organized clay homogeneously in a molten liquid raw material, a microstructure can be formed having an irregularly shaped resin phase continuous in a three-dimensional manner and having irregularly shaped pore

spaces therebetween, by cooling from an arbitrary melting temperature. With this microstructure, a satisfactory mechanical strength and permeation performance can be obtained by the continuous pore spaces and the continuous resin phase. Moreover, with use of the organized clay by a hydrophilic compound, a porous film of a poly(vinylidene fluoride) based resin with an improved hydrophilic property can be obtained.

[0012]

It is preferable that the temperature of said liquid raw material for a film before cooling is 170°C or above and lower than the thermal decomposition temperature of the poly(vinylidene fluoride) based resin. With this temperature range, the poly(vinylidene fluoride) based resin can be dissolved as a homogeneous phase, and the resin phase or the resin-concentrated phase is less liable to give an influence on the microstructure of the porous film, so that the control of the microstructure by the organized clay can be carried out with a higher precision.

[0013]

On the other hand, the porous film of the present invention is a porous film comprising a poly(vinylidene fluoride) based resin and an organized clay being organized by a hydrophilic compound, the organized clay being dispersed therein in an amount of 1 to 25 parts by weight relative to 100 parts by weight of the poly(vinylidene fluoride) based resin, wherein a microstructure is formed by a thermally induced phase separation method of cooling the liquid raw

material at temperature of 170°C or above, said microstructure having an irregularly shaped resin phase continuous in a three-dimensional manner with a network structure and having irregularly shaped pore spaces therebetween.

[0014]

When a porous film is formed by the wet-type film-forming method (non-solvent induced phase separation method) so as to attain nano dispersion of an organized clay in a poly(vinylidene fluoride) based resin, a microstructure is formed such as a sponge structure in which pore spaces having a shape near to a spherical shape are continuous in a three-dimensional manner or a finger void structure having finger-shaped macrovoids, and moreover, a pore diameter may be considerably different between the site near the film surface and the inside of the film. For this reason, mechanical strength such as tensile strength is liable to be insufficient. In contrast, with the present invention, by having the above-described microstructure which is a characteristic of a porous film formed by the thermally induced phase separation method, the porous film will have a satisfactory mechanical strength and permeation performance. Moreover, since an organized clay being organized by a hydrophilic compound is dispersed, the porous film will have an improved hydrophilic property.

CLAIMS

1.(Amended) A method for producing a porous film wherein a porous film of a poly(vinylidene fluoride) based resin is prepared by dissolving the poly(vinylidene fluoride) based resin in a poor solvent through heating to form a liquid raw material for a film, and then cooling the liquid raw material at temperature of 170°C or above to bring about a phase separation, characterized in that an organized clay being organized by a hydrophilic compound is dispersed in said liquid raw material for a film in an amount of 1 to 25 parts by weight relative to 100 parts by weight of the poly(vinylidene fluoride) based resin.

2. The method for producing a porous film according to claim 1, wherein the temperature of said liquid raw material for a film before cooling is 170°C or above and lower than the thermal decomposition temperature of the poly(vinylidene fluoride) based resin.

3. (Amended) A porous film comprising a poly(vinylidene fluoride) based resin and an organized clay being organized by a hydrophilic compound, the organized clay being dispersed therein in an amount of 1 to 25 parts by weight relative to 100 parts by weight of the poly(vinylidene fluoride) based resin, wherein a microstructure is formed by a thermally induced phase separation method of cooling

the liquid raw material at temperature of 170°C or above to bring about a phase separation, said microstructure having an irregularly shaped resin phase continuous in a three-dimensional manner with a network structure and having irregularly shaped pore spaces therebetween.

4. The porous film according to claim 3, wherein said organized clay is a clay prepared by organizing a layered inorganic silicate with an alkylene oxide compound.